

MATHEMATICAL MODELING OF UNSATURATED ISOPHTHALIC RESIN'S CURING CYCLE

RAVI KUMAR. V & PRAKASH. K. R

¹Department of Mechanical Engineering, Amrita School of Engineering, Bengaluru,
Amrita Vishwa Vidyapeetham, India

²Department of Mechanical Engineering, National Institute of Engineering, Mysore, India

ABSTRACT

Fiber reinforced plastics (FRP) products are light weighing and strong. These materials find extensive applications in various engineering fields and also as sensor material. Curing of this resin is a key to obtain FRP Products. Various factors including Gel time (T_{gel}) and peak exothermic temperature (T_{peak}) are the critical factors that directly affect the curing process. T_{gel} is the indicator for the commencement of setting (polymer cross-linking) while T_{peak} talks about the shrinkage and cracking of the polymer. This research work finds the T_{gel} and T_{peak} for the curing of UP resin based isophthalic acid. The Catalyst MEKP (methyl ethyl ketone peroxide). The accelerator cobalt octoate (Cost) were used for the curing process. Results showed strong interactions between the process variables mentioned above. The process was an optimization to achieve a combination of T_{gel} and T_{peak} within the regime of experimentation. Mathematical models were developed using regression for both peak temperature and gel time. Confirmatory experiments were performed to validate the predicted results.

KEYWORDS: Curing, Gel time, Peak exothermic temperature, ISO Resin, FRP, Process Optimization

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INTRODUCTION

One of the important thermoset resin is the unsaturated polyester resins which are basically macromolecules [1] with a polyester. The resin has medium viscosity. In specific the iso phthalic acid based resin shows excellent mechanical properties along with good chemical resistance. As any polyester resin, iso resin also has styrenes (45% to 48% by volume) as the monomer. In which the polyester molecule are dissolved. A peroxide compound, usually methyl ethyl ketone peroxide (MEKP) is used to catalyze the resin [2], which cross-links with some of the styrenes, but not all of it.

The UP resins shall be easily processed in filament winding hand layup process, resin transfer molding [3]. They can also widely used as a molding compound. Hence, these UP resins are used in a different fields like insulation coatings [4], widely used in making fiber reinforced plastics (FRP) products, plastic sandwich panels, pultrusion components [5,17] etc.

The curing process of UP resin happens due to chemical kinetics [6] and the same will be controlled by diffusion. The curing between styrene monomer and UP mainly occurs because of free radical chain -growth [7]. During this process at room temperature, the organic peroxides (like methyl ethyl ketone peroxide (MEKP)) are abundantly used as catalysts[8] Meanwhile cobalt salt is mostly used as an accelerator [8]. The inhibitors of

quinones and phenol [9] are mixed to react with the most of or propagating radicals [10] to reduce the effect of reactivity. This gives storage life [11]. The achievement of preparing an FRP product by a hand lay-up process [12] are mainly depends on the curing kinetics [14] and also the gel time. The complete interaction of chemical kinetics and physical phenomena like gelling process makes this curing process [15] highly complex [16].

MATERIALS AND EXPERIMENTAL SETUP

The resin used for the proposed work is a commercially available general purpose Unsaturated Polyester (UP) resin based on isophthalic acid formulated by Naptha Resins and Chemicals (P) Limited, India under the trade name 'Polyflex Gr 200-220'. The resin was found to have the properties as shown in table 1 below. The curing process consists of MEKP. This curing process was carried out at room temperature ($26 \pm 2^\circ\text{C}$) with a precalculated quantity of MEKP and Cost,. A cylindrical mold of diameter 67mm and height 36 mm made up of Stainless steel was used to complete the curing process. This device consists of a steel plunger oscillator which slides over the vertical column of the fixture which has the tapered end. In other hands the other end of the column is rested against a dial gauge to record the displacement of the plunger (depth of penetration). At this time, the reaction was started to turning to be stable condition. Figure 1, clearly shows the gel time indicator. We can also observe rise the temperature during curing process because of the exothermic reactions. This rise in temperature caused by this process successfully was monitored by using a thermocouple and the same was noted during this process. Figure2 shows a clear time-temperature graphs for the process.

Table 1: Properties of the Resin

Property	Value
Colour	Clear Liquid
Viscosity @ 25°C	540 cps
Acid value	10.46mg KOH/g
Volatile Content (2 g /150 $^\circ\text{C/hr}$)	39.36%
Gel Time @ 25°C Resin quantity 100 gms with 3% accelerator and 3% catalyst	12'35"



Figure 1: The Softness Indicator Setup

RESULTS AND DISCUSSIONS

Polymerization mechanism of UP resin with styrene as a cross-linking monomer is well known, which cleared that the UP resin is reacted with carbon-carbon covalent bonds, the same can be successfully cross-linked to form a sound thermosetting material. It is successfully achieved with the help of vinyl group molecules, namely styrenes in the good presence of MEKP catalyst and Cost accelerator. This process results in achieving a cross-link between the polymer chains and which results in the formation of a 3D, strong and sound polymer. The graphs below shows the variation of the temperature and penetration depth as a function of time for a few samples tested. Cross-linking mechanisms of polymer

chains were observed and recorded successfully which is shown in Table 2.

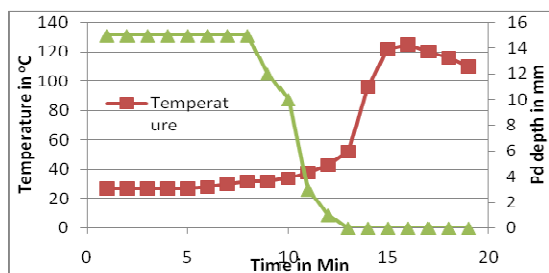


Figure 2(a): 4% cobalt and 5% MEKP

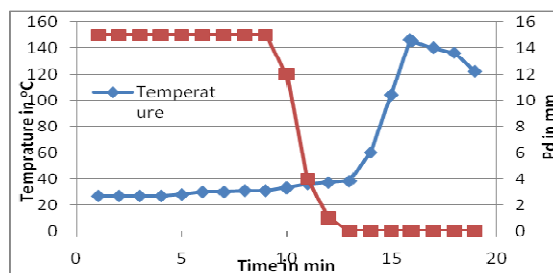


Figure 2(b): 5% Cobalt and 4% MEKP

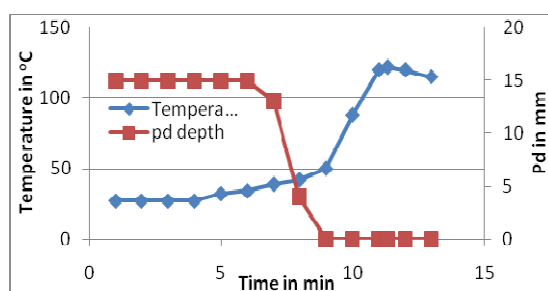


Figure 2(c): 5% Cobalt and 5% MEKP

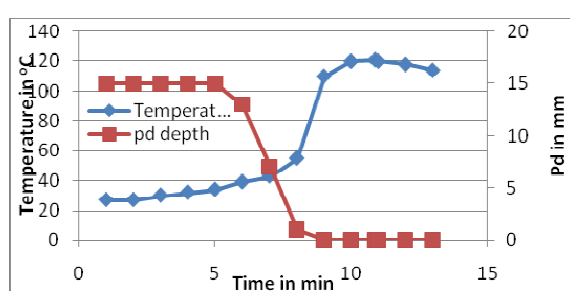


Figure 2(d) 5% Cobalt and 6% MEKP

Figure 2 a, b, c & d. Time – Temperature and penetration depth curves for different % of accelerator and catalyst.

Table 2: Peak Temp & Gel Time for Various Combination of Accelerator and Catalyst

Sl. No.	Accelerator as % wt	Hardener as % wt	Peak temp (°C)	Gel Time (Sec)
1	3	3	132	980
2	4	3	128	910
3	3	4	127	664
4	4	4	133	647
5	5	4	146	595
6	4	5	125	546
7	5	5	122	375
8	6	5	130	369
9	5	6	121	325
10	6	6	100	310
11	5	3	135	493
12	6	3	131	465
13	6	4	131	335
14	3	5	126	420
15	3	6	133	332
16	4	6	128	350

Figure 3. Is a surface graph representing an interaction between catalyst and accelerator with a decreasing trend in T_{gel} . T_{gel} is approximately 980 sec at the lowest levels (3%,3%) of catalyst and accelerator, which reduced to 310 sec at their highest levels (6%,6%). It can be clearly observed that for a taken level of accelerator concentration; the used catalyst results in a noticeable reduction in the T_{gel} . This is clearly because of increase in free radicals formed due to the decomposition of the catalyst with the help of accelerator. These free radicals formed during this process also the reason behind exothermic copolymerization reaction. During this process, the temperature rises. Also in other hands the

accumulation of heat energy results in increasing the rate of this reaction and rise in polymer molecular weight steadily.

From the bellow plots, we can clearly predict that for a taken level of catalyst, T_{gel} is very highly sensitive to use of low percentage of the accelerator and also confirms the sensitivity decreases to good extent and later it becomes almost constant for next percentage of an accelerator. This is claimed to be normal for a fixed level of catalyst controls the formation of free radicals that are the reason why we see an increasing trend at low percentages of an accelerator, as the catalyst is sufficient enough to produce free radicals by decomposition. The T_{gel} is less sensitive towards the increased percentage of accelerator this is due to the fact that the excess of accelerator present has already decomposed the catalyst available and hence decomposition has substantially completed, which intern means reduced levels of free radicals.

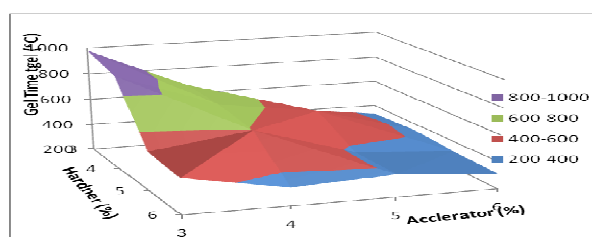


Figure 3: Surface Plot Showing Variation of gel Time as a Function of Accelerator and Catalyst(Hardner)

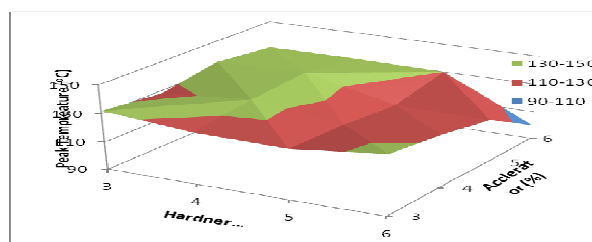


Figure 4: Surface Plot Showing Variation of Peak Temperature as a Function of Accelerator and Catalyst(Hardner)

Figure 4 above indicates the variation of the peak temperature with respect to the various combination of the accelerator and the catalyst. It can be noted that the increase in the accelerator levels does not contribute significantly towards the peak temperature at various levels of the catalyst. The higher the percentage of the catalyst the lesser is the peak temperature, i.e., the temperature reduces to 100°C at the highest levels of the catalyst.

Mathematical Model

A Mathematical model was developed to predict the Gel time for a different combination of Accelerator and Hardener. The summary output of the regression analysis is given below. The significance F is well below 0.05 which indicates that the considered parameters affect our measured output considerably and the P values for the different factors and their combination is less than 0.05 which means they are significant. The R square and Adjusted R square value is 90% which indicates that the mathematical model is close to the actual model and it can be further used to predict the Gel time for the different combination of Accelerator and Hardener. The mathematical model for Gel time is given below.

$$T_{gel} = 2749.42 - 370A - 412H + 63.28AH$$

Where A – Accelerator and H – Hardener

It was also observed that the predicted values are having less than 5% error.

SUMMARY	
Regression Statistics	
Multiple R	0.945370763
R Square	0.893725879
Adjusted R Square	0.867157349
Standard Error	75.42912788
Observations	16

ANOVA	df	SS	MS	F	Significance F
Regression	3	574164.36	191388.1	33.6385141	4.02781E-06
Residual	12	68274.64	5689.553		
Total	15	642439			

	Coefficients	Standard Error	t Stat	P-value	Lower 95%
Intercept	2749.42	324.3452499	8.476831	2.0685E-06	2042.732408
Accelerator as % wt	-370.16	69.95009554	-5.29177	0.00019089	-522.5681656
Hardener as % wt	-412.86	69.95009554	-5.90221	7.228E-05	-565.2681656
Acc*Hard	63.28	15.08582558	4.194666	0.00124364	30.41080969

In a similar manner, regression analysis was done for peak temperature. The following is the summary of the regression analysis done for peak temperature.

SUMMARY	
Regression Statistics	
Multiple R	0.722481257
R Square	0.521979167
Adjusted R Square	0.402473958
Standard Error	7.316989363
Observations	16

ANOVA	df	SS	MS	F	Significance F
Regression	3	701.54	233.8467	4.367836	0.026849984
Residual	12	642.46	53.53833		
Total	15	1344			

	Coefficients	Standard Error	t Stat	P-value	Lower 95%
Intercept	84.26	31.46305	2.678062	0.020109	15.70789372
Accelerator as % wt	13.87	6.785497	2.044066	0.063534	-0.914327458
Hardener as % wt	11.42	6.785497	1.683001	0.118189	-3.364327458
Acc*Hard	-3.46	1.463398	-2.36436	0.035767	-6.64847006

The mathematical model for peak temperature is given below.

$$T_{\text{peak}} = 84.26 + 13.87A + 11.42H - 3.46AH.$$

CONCLUSIONS

The lower T_{gel} value will result in defects like incomplete mold filling as at T_{gel} mobility is arrested in the polymer, while a higher value will increase the cycle time and reduce the productivity. Similarly, lower T_{peak} can slow down the reaction rate and hence have longer curing times, while the higher values may result in distortion of the part due to shrinkage and cracking. Thus the values of T_{gel} and T_{peak} , should be neither too less nor too high. This will ensure proper

curing cycles. Hence the values of both T_{gel} and T_{peak} play an important role in the curing process of a polymer composite. The preferred levels of this are around 600 sec that is 10 min for T_{gel} and 120°C for the T_{peak} . In this study hence an optimal percentage of catalyst and accelerator would be at 5% and 4 % respectively that has a peak temperature of around 125°C and 546 Sec. It is to be noted that the experiments of curing were conducted at room temperature.

REFERENCES

1. Sachin Waigankar, B J C Babu & Amit Rajpu (2011) Curing studies of unsaturated polyester resin used in FRP products. *Indian Journal of Engineering & Materials Sciences*. 18: 31-39
2. Piotr Penczek, Ewa Rudnik, Bogumiła Arczewska, Ryszard Ostrysz, (1995) Curing of unsaturated polyester resins with low exotherm peak *Polymer Science & Technology General*. 229:15-27
3. Nasr E S & Azim A (1992) A, *Polymer Advanced Technology*, 3: 407-411.
4. H. V. Boenig (1964), *Unsaturated Polyesters*, Elsevier Publ. Co., Amsterdam, p. 154
5. Yang H & Lee L J (2000). *J Appl Polym Sci*, Comparison of unsaturated polyester and vinyl ester resins in low temperature polymerization 79: 1230-1242.
6. V. Ravi Kumar, B. P. Dileep, and H. R. Vital; Tribological and mechanical characterization of Al-Ni-SiC metal matrix composites, *AIP Conference Proceedings* 1859 (2017), 020020.
7. Cook W D, Lau M, Mehrabi M, Dean K & Zipper M (2001) *Polym Int*, Control of gel time and exotherm behaviour during cure of unsaturated polyester resins, *Polymer International* 50: 129-134.
8. N. Naderi, S. Mazinani, M. Hosain Beheshty, M. Mahdi Rajab (2015) Cure kinetics of hot cured unsaturated polyester (UP)/nanoclay nanocomposite including dual initiators, *Plastics, Rubber and Composites*, 44 : 19-25
9. Ζασκε Ο Ψ & Γκοδμάν Σ Η (2005). *Hand Book of Thermoset Plastics*. Jaico Publishing House, India.
10. Fried J R (2005). *Polymer Science & Technology*, Pearson Education, India.
11. Dyson R W (1998). *Specialty Polymers*, 2nd ed. Blackie Academic & Professional, UK.
12. M.-J. Brekner and C. Feger (2003) Curing studies of a polyimide precursor. *Journal of Polymer Science Part A: Polymer Chemistry* 25: 7
13. T. Maity, B. C. Samanta, S. Dalai, A. K. Banthia, (2007) "Synthesis, characterisation and curing studies of BCCOMB", *Pigment & Resin Technology*, 36: 30 – 38
14. Lakshmi. B, Shivananda. K. N, Mahendra. K. N. (2010) Synthesis, Characterization and Curing Studies of Thermosetting Epoxy Resin with Amines Department of Studies in Chemistry. *Korean Chem. Soc.* 31: 2272 – 2278
15. V. Ravi Kumar, B. P. Dileep, S. Mohan Kumar, and M. V. Phanibhushana, Effect of metal coatings on mechanical properties of alluminium alloy, *AIP Conference Proceedings* 1859 (2017), 020037-1 – 020037-6.
16. Dileep, B. P., Ravi Kumar, V. Prashanth Mrudula, and M. V. Phanibhushana, "Effect of zinc coating on mechanical properties of Al 7075", in *Applied Mechanics and Materials*, 592-594, 2014 pp, 255-259
17. Dileep B P, B, R, Sridhar, "A Investigation on Mechanical and Metallurgical Properties of Steel EN24 and SiC MMCs, *International Journal of Mechanical and Production Engineering Research and Development (IJMPERD)*, Vol. 8, Issue 2, Apr 2018, 189-194